PATENT COOPERATION TREATY

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

To:

Commissioner
US Department of Commerce
United States Patent and Trademark Office, PCT
2011 South Clark Place Room CP2/5C24
Arlington, VA 22202
ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

Date of mailing (day/month/year) 03 October 2001 (03.10.01)	
International application No. PCT/US00/29147	**Applicant's or agent's file reference** DP-301411 PCT
International filing date (day/month/year) 20 October 2000 (20.10.00)	**Priority date** (day/month/year) 20 October 1999 (20.10.99)
Applicant DETWILER, Eric, J. et al	

1. The designated Office is hereby notified of its election made:

[X] in the demand filed with the International Preliminary Examining Authority on:

17 May 2001 (17.05.01)

[ ] in a notice effecting later election filed with the International Bureau on:

2. The election [X] was

[ ] was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO **34, chemin des Colombettes** **1211 Geneva 20, Switzerland**	Authorized officer Pascal Piriou
Facsimile No.: (41-22) 740.14.35	Telephone No.: (41-22) 338.83.38

PCT

REQUEST

The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty.

, receiving Office use only

International Application No.

International Filing Date

Name of receiving Office and "PCT International Application"

Applicant's or agent's file reference *(if desired) (12 characters maximum)* DP-301411 PCT

Box No. I TITLE OF INVENTION

GAS SENSOR DESIGN AND METHOD FOR USING THE SAME

Box No. II APPLICANT

Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)*

DELPHI TECHNOLOGIES, INC.
Legal Staff MC 480-414-420
1450 West Long Lake Road
Troy, MI 48007-5052
US

☐ This person is also inventor.

Telephone No.
(248) 267-5513

Facsimile No.
(248) 267-5559

Teleprinter No.

State *(that is, country)* of nationality:
US

State *(that is, country)* of residence:
US

This person is applicant for the purposes of: ☒ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)

Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)*

DETWILER, Eric J.
1518 Colleen Lane
Davison, MI 48423
US

This person is:

☐ applicant only

☒ applicant and inventor

☐ inventor only *(If this check-box is marked, do not fill in below.)*

State *(that is, country)* of nationality:

State *(that is, country)* of residence:

This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☒ the United States of America only ☐ the States indicated in the Supplemental Box

☒ Further applicants and/or (further) inventors are indicated on a continuation sheet.

Box No. IV AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE

The person identified below is hereby/has been appointed to act on behalf of the applicant(s) before the competent International Authorities as: ☒ agent ☐ common representative

Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)*

CURBELO, Pamela J.
CANTOR COLBURN LLP
55 Griffin Road South
Bloomfield, CT 06002
US

Telephone No.
(860) 286-2929

Facsimile No.
(860) 286-0115

Teleprinter No.

☐ **Address for correspondence:** Mark this check-box where no agent or common representative is/has been appointed and the space above is used instead to indicate a special address to which correspondence should be sent.

Continuation of Box No. III FURTHER APPLICANTS AND/OR (FURTHER) INVENTOR(S)

If none of the following sub-boxes is used, this sheet is not to be included in the request.

Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)*

COHA, Jeffrey T.
5483 Maple Park Drive
Flint, MI 48507
US

This person is:
- ☐ applicant only
- ☒ applicant and inventor
- ☐ inventor only *(If this check-box is marked, do not fill in below.)*

State *(that is, country)* of nationality:

State *(that is, country)* of residence:

This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☒ the United States of America only ☐ the States indicated in the Supplemental Box

Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)*

WANG, Da Yu
2188 Lancer Drive
Troy, MI 48084
US

This person is:
- ☐ applicant only
- ☒ applicant and inventor
- ☐ inventor only *(If this check-box is marked, do not fill in below.)*

State *(that is, country)* of nationality:

State *(that is, country)* of residence:

This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☒ the United States of America only ☐ the States indicated in the Supplemental Box

Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)*

This person is:
- ☐ applicant only
- ☐ applicant and inventor
- ☐ inventor only *(If this check-box is marked, do not fill in below.)*

State *(that is, country)* of nationality:

State *(that is, country)* of residence:

This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

Name and address: *(Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)*

This person is:
- ☐ applicant only
- ☐ applicant and inventor
- ☐ inventor only *(If this check-box is marked, do not fill in below.)*

State *(that is, country)* of nationality:

State *(that is, country)* of residence:

This person is applicant for the purposes of: ☐ all designated States ☐ all designated States except the United States of America ☐ the United States of America only ☐ the States indicated in the Supplemental Box

☐ Further applicants and/or (further) inventors are indicated on another continuation sheet.

Box No.V DESIGNATION OF STATES

The following designations are hereby made under Rule 4.9(a) *(mark the applicable check-boxes; at least one must be marked):*

Regional Patent

☐ **AP ARIPO Patent:** **GH** Ghana, **GM** Gambia, **KE** Kenya, **LS** Lesotho, **MW** Malawi, **MZ** Mozambique, **SD** Sudan, **SL** Sierra Leone, **SZ** Swaziland, **TZ** United Republic of Tanzania, **UG** Uganda, **ZW** Zimbabwe, and any other State which is a Contracting State of the Harare Protocol and of the PCT

☐ **EA Eurasian Patent:** **AM** Armenia, **AZ** Azerbaijan, **BY** Belarus, **KG** Kyrgyzstan, **KZ** Kazakhstan, **MD** Republic of Moldova, **RU** Russian Federation, **TJ** Tajikistan, **TM** Turkmenistan, and any other State which is a Contracting State of the Eurasian

☒ **EP European Patent:** **AT** Austria, **BE** Belgium, **CH and LI** Switzerland and Liechtenstein, **CY** Cyprus, **DE** Germany, **DK** Denmark, **ES** Spain, **FI** Finland, **FR** France, **GB** United Kingdom, **GR** Greece, **IE** Ireland, **IT** Italy, **LU** Luxembourg, **MC** Monaco, **NL** Netherlands, **PT** Portugal, **SE** Sweden, and any other State which is a Contracting State of the European Patent Convention and of the PCT

☐ **OA OAPI Patent:** **BF** Burkina Faso, **BJ** Benin, **CF** Central African Republic, **CG** Congo, **CI** Côte d'Ivoire, **CM** Cameroon, **GA** Gabon, **GN** Guinea, **GW** Guinea-Bissau, **ML** Mali, **MR** Mauritania, **NE** Niger, **SN** Senegal, **TD** Chad, **TG** Togo, and any other State which is a member State of OAPI and a Contracting State of the PCT *(if other kind of protection or treatment desired, specify on dotted line)* .....

National Patent *(if other kind of protection or treatment desired, specify on dotted line):*

☐ **AE** United Arab Emirates
☐ **AG** Antigua and Barbuda
☐ **AL** Albania .....
☐ **AM** Armenia .....
☐ **AT** Austria .....
☐ **AU** Australia .....
☐ **AZ** Azerbaijan
☐ **BA** Bosnia and Herzegovina .....
☐ **BB** Barbados
☐ **BG** Bulgaria .....
☐ **BR** Brazil .....
☐ **BY** Belarus .....
☐ **BZ** Belize
☐ **CA** Canada
☐ **CH and LI** Switzerland and Liechtenstein
☐ **CN** China .....
☐ **CR** Costa Rica .....
☐ **CU** Cuba .....
☐ **CZ** Czech Republic .....
☐ **DE** Germany .....
☐ **DK** Denmark .....
☐ **DM** Dominica
☐ **DZ** Algeria .....
☐ **EE** Estonia .....
☐ **ES** Spain .....
☐ **FI** Finland .....
☐ **GB** United Kingdom
☐ **GD** Grenada
☐ **GE** Georgia .....
☐ **GH** Ghana .....
☐ **GM** Gambia
☐ **HR** Croatia .....
☐ **HU** Hungary .....
☐ **ID** Indonesia
☐ **IL** Israel .....
☐ **IN** India .....
☐ **IS** Iceland
☒ **JP** Japan .....
☐ **KE** Kenya .....
☐ **KG** Kyrgyzstan .....
☐ **KP** Democratic People's Republic of Korea .....
☐ **KR** Republic of Korea .....
☐ **KZ** Kazakhstan .....
☐ **LC** Saint Lucia
☐ **LK** Sri Lanka
☐ **LR** Liberia
☐ **LS** Lesotho .....
☐ **LT** Lithuania
☐ **LU** Luxembourg
☐ **LV** Latvia
☐ **MA** Morocco .....
☐ **MD** Republic of Moldova .....
☐ **MG** Madagascar .....
☐ **MK** The former Yugoslav Republic of Macedonia .....
☐ **MN** Mongolia
☐ **MW** Malawi .....
☐ **MX** Mexico .....
☐ **MZ** Mozambique
☐ **NO** Norway
☐ **NZ** New Zealand .....
☐ **PL** Poland .....
☐ **PT** Portugal .....
☐ **RO** Romania
☐ **RU** Russian Federation .....
☐ **SD** Sudan
☐ **SE** Sweden
☐ **SG** Singapore
☐ **SI** Slovenia .....
☐ **SK** Slovakia .....
☐ **SL** Sierra Leone .....
☐ **TJ** Tajikistan .....
☐ **TM** Turkmenistan .....
☐ **TR** Turkey .....
☐ **TT** Trinidad and Tobago .....
☐ **TZ** United Republic of Tanzania
☐ **UA** Ukraine .....
☐ **UG** Uganda .....
☒ **US** United States of America .....
☐ **UZ** Uzbekistan .....
☐ **VN** Viet Nam .....
☐ **YU** Yugoslavia .....
☐ **ZA** South Africa .....
☐ **ZW** Zimbabwe .....

Check-boxes reserved for designating States which have become party to the PCT after issuance of this sheet:

☐ .....

Precautionary Designation Statement: In addition to the designations made above, the applicant also makes under Rule 4.9(b) all other designations which would be permitted under the PCT except any designation(s) indicated in the Supplemental Box as being excluded from the scope of this statement. The applicant declares that those additional designations are subject to confirmation and that any designation which is not confirmed before the expiration of 15 months from the priority date is to be regarded as withdrawn by the applicant at the expiration of that time limit. *(Confirmation (including fees) must reach the receiving Office within the 15-month time limit.)*

Box No. VI PRIORITY CLAIM ☐ Further priority claims are indicated in the Supplemental Box.

Filing date of earlier application (day/month/year)	Number of earlier application	Where earlier application is: national application: country	regional application:* regional Office	international application: receiving Office
item (1) 20 October 1999 (20.10.99)	60/160,733	US		
item (2)				
item (3)				

☒ The receiving Office is requested to prepare and transmit to the International Bureau a certified copy of the earlier application(s) *(only if the earlier application was filed with the Office which for the purposes of the present international application is the receiving Office)* identified above as item(s): (1)

* *Where the earlier application is an ARIPO application, it is mandatory to indicate in the Supplemental Box at least one country party to the Paris Convention for the Protection of Industrial Property for which that earlier application was filed (Rule 4.10(b)(ii)). See Supplemental Box.*

Box No. VII INTERNATIONAL SEARCHING AUTHORITY

Choice of International Searching Authority (ISA) *(if two or more International Searching Authorities are competent to carry out the international search, indicate the Authority chosen; the two-letter code may be used):*

ISA/EP

Request to use results of earlier search; reference to that search *(if an earlier search has been carried out by or requested from the International Searching Authority):*

Date *(day/month/year)* Number Country *(or regional Office)*

Box No. VIII CHECK LIST: LANGUAGE OF FILING

This international application contains the following **number of sheets:**

request	:	4
description (excluding sequence listing part)	:	14
claims	:	3
abstract	:	1
drawings	:	2
sequence listing part of description	:	
Total number of sheets	:	24

This international application is **accompanied** by the item(s) marked below:

1. ☒ fee calculation sheet
2. ☐ separate signed power of attorney
3. ☒ copy of general power of attorney; reference number, if any:
4. ☐ statement explaining lack of signature
5. ☐ priority document(s) identified in Box No. VI as item(s):
6. ☐ translation of international application into (language):
7. ☐ separate indications concerning deposited microorganism or other biological material
8. ☐ nucleotide and/or amino acid sequence listing in computer readable form
9. ☒ other *(specify):* Transmittal Letter

Figure of the drawings which should accompany the abstract: 2

Language of filing of the international application: English

Box No. IX SIGNATURE OF APPLICANT OR AGENT

Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the request).

Pamela J. Curbelo
Applicant's Attorney

For receiving Office use only

1. Date of actual receipt of the purported international application:
3. Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application:
4. Date of timely receipt of the required corrections under PCT Article 11(2):
5. International Searching Authority (if two or more are competent): ISA/
6. ☐ Transmittal of search copy delayed until search fee is paid.

2. Drawings:
☐ received:
☐ not received:

For International Bureau use only

Date of receipt of the record copy by the International Bureau:

This sheet is not part of and does not count as a sheet of the international application.

PCT

FEE CALCULATION SHEET

Annex to the Request

For receiving Office use only

International application No.

Date stamp of the receiving Office

Applicant's or agent's file reference: DP-301411 PCT

Applicant: DELPHI TECHNOLOGIES, INC.

CALCULATION OF PRESCRIBED FEES

1. TRANSMITTAL FEE . . . . . 240.00 T

2. SEARCH FEE . . . . . 925.00 S

International search to be carried out by ISA/EP

(If two or more International Searching Authorities are competent in relation to the international application, indicate the name of the Authority which is chosen to carry out the international search.)

3. INTERNATIONAL FEE

Basic Fee

The international application contains 24 sheets.

first 30 sheets 427.00 b1

0 (remaining sheets) x _____ (additional amount) = 0.00 b2

Add amounts entered at b1 and b2 and enter total at B . . 427.00 B

Designation Fees

The international application contains 3 designations.

3 (number of designation fees payable *(maximum 8)*) x 92.00 (amount of designation fee) = 276.00 D

Add amounts entered at B and D and enter total at I . . . . . 703.00 I

(Applicants from certain States are entitled to a reduction of 75% of the international fee. Where the applicant is (or all applicants are) so entitled, the

4. FEE FOR PRIORITY DOCUMENT *(if applicable)* . . . . . 15.00 P

5. TOTAL FEES PAYABLE . . . . . 1,883.00 TOTAL

Add amounts entered at T, S, I and P, and enter total in the TOTAL box

☐ The designation fees are not paid at this time.

MODE OF PAYMENT

☒ authorization to charge deposit account (see below)
☐ bank draft
☐ coupons
☐ cheque
☐ cash
☐ other *(specify):*
☐ postal money order
☐ revenue stamps

DEPOSIT ACCOUNT AUTHORIZATION *(this mode of payment may not be available at all receiving Offices)*

The RO/ US

☒ is hereby authorized to charge the total fees indicated above to my deposit account.

☒ *(this check-box may be marked only if the conditions for deposit accounts of the receiving Office so permit)* is hereby authorized to charge any deficiency or credit any overpayment in the total fees indicated above to my deposit account.

☐ is hereby authorized to charge the fee for preparation and transmittal of the priority document to the International Bureau of WIPO to my deposit account.

06-1130	20 Oct ber 2000 (20.10.00)	
Deposit Account No.	Date *(day/month/year)*	Signature

PCT

GENERAL POWER OF ATTORNEY

(for several international applications filed under the Patent Cooperation Treaty)

(PCT Rule 90.5)

The undersigned person(s) :
(Family name followed by given name: for a legal entity, full official designation. The address must include postal code and name of country.)

ASEC MANUFACTURING PARTNERSHIP

hereby appoint(s) the following person as: [X] agent [ ] common representative

Name and address
(Family name followed by given name: for a legal entity, full official designation. The address must include postal code and name of country.)

Cichosz, Vincent A.
Delphi Technologies, Inc.
Legal Staff MC 480-414-420
P.O. Box 5052
Troy, MI 48007-5052
United States of America

to represent the undersigned before

[X] all the competent International Authorities
[ ] the International Searching Authority only
[ ] the International Preliminary Examining Authority only

in connection with any and all international applications filed by the undersigned with the following Office

United States Patent and Trademark Office as receiving Office
and to make or receive payments on behalf of the undersigned.

Signature(s) *(where there are several persons, each of them must sign; next to each signature, indicate the name of the person signing and the capacity in which the person signs, if such capacity is not obvious from reading this power)*:

Guy Jones, Managing Director of Partnership

Date: 1/13/00

PCT

GENERAL POWER OF ATTORNEY

(for several international applications filed under the Patent Cooperation Treaty)

(PCT Rule 90.5)

The undersigned person(s):
(Family name followed by given name: for a legal entity, full official designation. The address must include postal code and name of country.)

CICHOSZ, Vincent A.
Delphi Technologies, Inc.
Legal Staff MC 480-414-420
1450 W. Long Lake Road
Troy, Michigan 48007-5052
United States of America

hereby appoint(s) the following person as: [X] agent [ ] common representative

Name and address
(Family name followed by given name: for a legal entity, full official designation. The address must include postal code and name of country.)

CANTOR, Michael A., Reg. No. 31,152;
MURPHY, Keith J., Reg. No. 33,979;
FOX, David A., Reg. No. 38,807;
CURBELO, Pamela J., Reg. No. 34,676;
BEDINGFIELD, Herbert M., Reg.No.44,530;
LYMAN, George J., Reg. No. 44,884;
COLBURN II, Philmore H., Reg. No.35,101;
REITER, Leah M., Reg. No. 39.341;
ELLIS, Edward J., Reg. No. 40,389;
VILLAR, Juan C., Reg. No. 34,271;
OLSON, Timothy B., Reg. No. 42,962;
Address: CANTOR COLBURN LLP
55 Griffin Road South
Bloomfield, CT 06002
US

to represent the undersigned before

[X] all the competent International Authorities
[X] the International Searching Authority only
[X] the International Preliminary Examining Authority only

in connection with any and all international applications filed by the undersigned with the following Office

United States Patent & Trademark Office as receiving Office

and to make or receive payments on behalf of the undersigned.

Signature(s) *(where there are several persons, each of them must sign: next to each signature, indicate the name of the person signing and the capacity in which the person signs, if such capacity is not obvious from reading this power):*

Vincent A. Cichosz, Agent

Date: July 31, 2000

Form PCT/Model of general power of attorney (for several international applications) (July 1992)

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference	**FOR FURTHER ACTION**	see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.
DP-301411 PCT		
International application No.	International filing date *(day/month/year)*	(Earliest) Priority Date *(day/month/year)*
PCT/US 00/ 29147	20/10/2000	20/10/1999
Applicant		
DELPHI TECHNOLOGIES, INC. et al.		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 2 sheets.

[X] It is also accompanied by a copy of each prior art document cited in this report.

1. **Basis of the report**

   a. With regard to the **language,** the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.

   [ ] the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

   b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :

   [ ] contained in the international application in written form.

   [ ] filed together with the international application in computer readable form.

   [ ] furnished subsequently to this Authority in written form.

   [ ] furnished subsequently to this Authority in computer readble form.

   [ ] the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

   [ ] the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. [ ] **Certain claims were found unsearchable** (See Box I).

3. [ ] **Unity of invention is lacking** (see Box II).

4. With regard to the **title,**

   [X] the text is approved as submitted by the applicant.

   [ ] the text has been established by this Authority to read as follows:

5. With regard to the **abstract,**

   [X] the text is approved as submitted by the applicant.

   [ ] the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No. 2

   [X] as suggested by the applicant.

   [ ] because the applicant failed to suggest a figure.

   [ ] because this figure better characterizes the invention.

   [ ] None of the figures.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 00/29147

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 G01N27/407

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 G01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	DE 198 35 766 A (BOSCH GMBH ROBERT) 17 February 2000 (2000-02-17) column 2, line 29 - line 38; figure 3 abstract	1,12
A	US 5 304 294 A (WANG DA Y ET AL) 19 April 1994 (1994-04-19) abstract column 2, line 18 - line 53; figure 1	1-20
A	US 4 657 659 A (MASE SYUNZO ET AL) 14 April 1987 (1987-04-14) abstract column 4, line 9 - line 43; figure 1	1-20

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
29 January 2001	06/02/2001

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Kempf, G

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 00/29147

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 19835766 A	17-02-2000	JP 2000055872 A	25-02-2000
US 5304294 A	19-04-1994	US 5217588 A	08-06-1993
		DE 4305412 A	16-09-1993
		JP 6018480 A	25-01-1994
US 4657659 A	14-04-1987	JP 1880381 C	21-10-1994
		JP 6005222 B	19-01-1994
		JP 61256251 A	13-11-1986

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

3

Applicant's or agent's file reference DP-301411PCT	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. PCT/US00/29147	International filing date (day/month/year) 20 OCTOBER 2000	Priority date (day/month/year) 20 OCTOBER 1999
International Patent Classification (IPC) or national classification and IPC IPC(7): G01N 27/407 and US Cl.: 204/424		
Applicant DELPHI TECHNOLOGIES, INC.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 5 sheets.

   ☐ This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority. (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of 0 sheets.

3. This report contains indications relating to the following items:

   - I ☒ Basis of the report
   - II ☐ Priority
   - III ☐ Non-establishment of report with regard to novelty, inventive step or industrial applicability
   - IV ☐ Lack of unity of invention
   - V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
   - VI ☒ Certain documents cited
   - VII ☐ Certain defects in the international application
   - VIII ☐ Certain observations on the international application

Date of submission of the demand	Date of completion of this report
17 MAY 2001	14 MARCH 2002
Name and mailing address of the IPEA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer T. TUNG Telephone No. (703) 308-3329

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.
PCT/US00/29147

I. Basis of the report

1. With regard to the **elements** of the international application:*

[X] the international application as originally filed

[X] the description:
pages 1-14 , as originally filed
pages NONE , filed with the demand
pages NONE , filed with the letter of _____

[X] the claims:
pages 15-17 , as originally filed
pages NONE , as amended (together with any statement) under Article 19
pages NONE , filed with the demand
pages NONE , filed with the letter of _____

[X] the drawings:
pages 1-2 , as originally filed
pages NONE , filed with the demand
pages NONE , filed with the letter of _____

[X] the sequence listing part of the description:
pages NONE , as originally filed
pages NONE , filed with the demand
pages NONE , filed with the letter of _____

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.
These elements were available or furnished to this Authority in the following language _____ which is:

[ ] the language of a translation furnished for the purposes of international search (under Rule 23.1(b)).

[ ] the language of publication of the international application (under Rule 48.3(b)).

[ ] the language of the translation furnished for the purposes of international preliminary examination (under Rules 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

[ ] contained in the international application in printed form.

[ ] filed together with the international application in computer readable form.

[ ] furnished subsequently to this Authority in written form.

[ ] furnished subsequently to this Authority in computer readable form.

[ ] The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

[ ] The statement that the information recorded in computer readable form is identical to the writen sequence listing has been furnished.

4. [X] The amendments have resulted in the cancellation of:

[X] the description, pages NONE

[X] the claims, Nos. NONE

[X] the drawings, sheets/~~fig~~ NONE

5. [ ] This report has been drawn as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).**

** Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17).*

***Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.*

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.
PCT/US00/29147

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. statement

Novelty (N)	Claims	4,5,7-9 and 12-20	YES
	Claims	1-3,6,10 and 11	NO
Inventive Step (IS)	Claims	NONE	YES
	Claims	1-20	NO
Industrial Applicability (IA)	Claims	1-20	YES
	Claims	NONE	NO

2. citations and explanations (Rule 70.7)

Claims 1-3,6, 10 and 11 lack novelty over Sasayama et al under PCT article 33(2).

Sasayama discloses a reference electrode 12 with a portion of its surface area exposed to a reference gas channel 32. The exposed portion is less than about 50% of the entire surface area. There is another electrode 19 with a surface area smaller than that of electrode 12. See figure 8; column 5, line 50 to column 6, line 13.

Claims 1-3 and 6 lack novelty over Mase etal under PCT Article 33(2).

Mase discloses a reference electrode with a portion of its surface area exposed to a reference gas channel 7,7'. The exposed portion is less than about 50% of the entire surface area. See particularly figure 4; column 4, line 20 to column 5, line 55.

Claims 4,5 and 7-9 lack an inventive step over Sasayama etal or Mase etal under PCT article 33(3).

Claims 4 and 5 differ by calling for the exposed portion of the surface area to be less than about 25%, while claims 7-9 differ by calling for a sensor impedance of 3400 ohms to 4000 ohms.

In the absence of unexpected result, it would have been obvious to provide a reference electrode with an exposed portion of less than 25%.

Also, solid electrolyte sensors conventionally have impedance values in the range recited by applicant. It would have been obvious for Sasayama or Mase to adopt such impedance values in the absence of unexpected result.

Claims 12-20 lack an inventive step over Sasayama etal or Mase etal in view of Schneider etal or Wiedenmann etal under PCT article 33(3).

These claims differ by calling for the formation of a reference gas channel by providing a fugitive material which is burned out by sintering.

Schneider (column 4, line 26 to column 5, line 30) or Wiedenmann (column 6, lines 44-56; column 7, line 60 to column 8, line 40) discloses burning out a fugitive material by sintering (Continued on Supplemental Sheet.)

VI. Certain documents cited

1. Certain published documents (Rule 70.10)

Application No. Patent No.	Publication Date (day/month/year)	Filing Date (day/month/year)	Priority date (valid claim) (day/month/year)
US 5,976,350	02 NOVEMBER 1999	29 AUGUST 1997	29 AUGUST 1996
US 6,287,439	11 SEPTEMBER 2001	15 MAY 1998	20 MAY 1997

2. Non-written disclosures (Rule 70.9)

Kind of non-written disclosure	Date of non-written disclosure (day/month/year)	Date of written disclosure referring to non-written disclosure (day/month/year)

Supplemental Box
(To be used when the space in any of the preceding boxes is not sufficient)

Continuation of: Boxes I - VIII

V. 2. REASONED STATEMENTS - CITATIONS AND EXPLANATIONS (Continued):
to form a diffusion channel. It would have been obvious for Sasayama or Mase to adopt this technique of Schneider or Wiedenmann to form its reference gas channel in the absence of unexpected result.

---------- NEW CITATIONS ----------

US 4,655,901 A (MASE ET AL) 07 April 1987, see figures 1-4 column 4, line 20 to column 5, line 55.

US 4,900,425 A (SASAYAMA ET AL) 13 February 1990, see figure 8; column 5, line 50 to column 6, line 13.

US 5,169,512 A (WIEDENMANN ETAL) 08 December 1992, see column 6, lines 44-56; column 7, line 60 to column 8, line 40.

US 5,529,677 A (SCHNEIDER ETAL) 25 June 1996, see column 4, line 26 to column 5, line 30.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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60/160,733 20 October 1999 (20.10.1999) US

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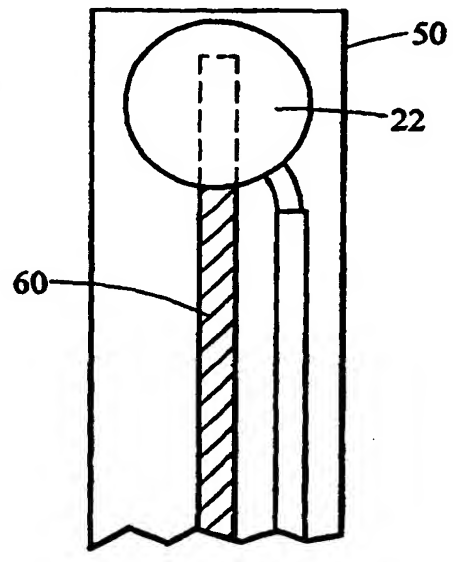
Published:
— *With international search report.*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: GAS SENSOR DESIGN AND METHOD FOR USING THE SAME



(57) **Abstract:** A gas sensor comprises a first electrode and a reference electrode with an electrolyte disposed therebetween, wherein the first electrode and said reference electrode are in ionic communication, wherein the reference electrode has a surface on a side of the reference electrode opposite the electrolyte and the surface has a surface area. The gas sensor also comprises a reference gas channel in fluid communication with the reference electrode, wherein at least a portion of the surface of the reference electrode physically contacts at least a portion of the reference gas channel, and wherein the portion of the reference electrode in physical contact with the reference gas channel is less than about 90 % of the surface area.

WO 01/29552 A1

GAS SENSOR DESIGN AND METHOD FOR USING THE SAME

CROSS REFERENCE TO RELATED APPLICATIONS

This case claims the benefit of the filing date of the provisional application U.S. Provisional Application Serial No. 60/160,733 filed October 20, 1999, which is hereby incorporated by reference in its entirety.

TECHNICAL FIELD

This invention relates to gas sensors, and, more particularly, to oxygen sensors.

BACKGROUND OF THE INVENTION

Oxygen sensors are used in a variety of applications that require qualitative and quantitative analysis of gases. In automotive applications, the direct relationship between the oxygen concentration in the exhaust gas and the air-to-fuel ratio of the fuel mixture supplied to the engine allows the oxygen sensor to provide oxygen concentration measurements for determination of optimum combustion conditions, maximization of fuel economy, and the management of exhaust emissions.

A conventional stoichiometric oxygen sensor typically comprises an ionically conductive solid electrolyte material, a porous electrode on the exterior surface of the electrolyte exposed to the exhaust gases with a porous protective overcoat, and an electrode on the interior surface of the sensor exposed to a known oxygen partial pressure. Sensors typically used in automotive applications use a yttria stabilized zirconia based electrochemical galvanic cell with platinum electrodes, which operate in potentiometric mode to detect the relative amounts of oxygen present in the exhaust of an automobile engine. When opposite surfaces of this galvanic cell are exposed to different oxygen partial pressures, an electromotive force is developed between the electrodes on the opposite surfaces of the zirconia wall, according to the Nernst equation:

$$E = \left(\frac{RT}{4F}\right) \ln\left(\frac{P_{O_2}^{ref}}{P_{O_2}}\right)$$

where:

E	=	electromotive force
R	=	universal gas constant
F	=	Faraday constant
T	=	absolute temperature of the gas
$P_{O_2}^{ref}$	=	oxygen partial pressure of the reference gas
P_{O_2}	=	oxygen partial pressure of the exhaust gas

Due to the large difference in oxygen partial pressure between fuel rich and fuel lean exhaust conditions, the electromotive force (emf) changes sharply at the stoichiometric point, giving rise to the characteristic switching behavior of these sensors. Consequently, these potentiometric oxygen sensors indicate qualitatively whether the engine is operating fuel-rich or fuel-lean, conditions without quantifying the actual air-to-fuel ratio of the exhaust mixture.

The internal resistance of a gas sensor significantly impacts the sensors performance. Areas affected include: light off time, steady state offset voltage, voltage output levels, and "loading down" effect of input impedance. The internal resistance of a gas sensor is comprised of three components: the linear electrolyte resistance, the nonlinear reference electrode polarization (overpotential), and the exhaust gas electrode polarization (overpotential). The first two components play a dominant role in the internal resistance, while the exhaust gas electrode polarization is not as important.

The linear electrolyte resistance and the nonlinear reference electrode polarization affect sensor performance because of the high electrical charge exchange rate with the electrolyte when platinum is used as the electrode material. Because of this, the size of the electrodes, particularly the reference electrode plays an important role in determining the overall impedance of the sensor. Conventional reference electrodes are manufactured as large as the air reference chamber (as large as possible) due to the fear that the electrode would polarize due to diffusion limiting. Therefore, the impedance of the sensor would be large due to the small reference electrode.

Other sensor designs have attempted to lower the impedance of the sensor by having dual lower shields, a higher wattage heater, a lower mass element, or by reducing the zirconia thickness. However, although these methods reduce impedance, these processes are limited and tend to affect sensor performance.

What is needed in the art is an improved reference electrode that reduces impedance.

BRIEF SUMMARY OF THE INVENTION

The deficiencies of the above-discussed prior art are overcome or alleviated by the gas sensor and method of producing the same.

In a preferred embodiment, a gas sensor comprises a first electrode and a reference electrode with an electrolyte disposed therebetween, wherein the first electrode and said reference electrode are in ionic communication, wherein the reference electrode has a surface on a side of the reference electrode opposite the electrolyte and the surface has a surface area. The gas sensor also comprises a reference gas channel in fluid communication with the reference electrode, wherein at least a portion of the surface of the reference electrode physically contacts at least a portion of the reference gas channel, and wherein the portion of the reference electrode in physical contact with the reference gas channel is less than about 90% of the surface area.

In a preferred method, a gas sensor is formed by disposing an outer electrode and a reference electrode on opposite sides of an electrolyte such that the outer electrode and the reference electrode are in ionic communication, wherein the reference electrode has a surface on a side of the reference electrode opposite the electrolyte. Disposing at least a portion of a fugitive material in physical contact with a portion of the reference electrode surface, wherein the reference electrode has a surface area and the portion of the reference electrode surface in physical contact with the fugitive material is less than about 90% of the surface area. Disposing a heater on a side of the fugitive material opposite the reference electrode to form a green sensor and co-firing the green sensor.

The above-described and other features and advantages of the present invention will be appreciated and understood by those skilled in the art from the following detailed description, drawings, and appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

The apparatus and method will now be described by way of example, with reference to the accompanying drawing, which is meant to be exemplary, not limiting.

Figure 1 is an expanded view of a sensor design.

Figure 2 is a view of a exemplary design of a reference electrode and a reference gas channel.

Figure 3 is a cross-sectional view of a sensor design.

Figure 4 is a circuit diagram for a sensor.

Figure 5 is a graphical representation of sensor resistance in comparison to model resistance over a range of temperatures

DETAILED DESCRIPTION OF THE INVENTION

Although the gas sensor will be described in relation to an oxygen sensor, it is understood that the novelties disclosed herein can be applied to any gas sensor, including, but not limited to nitrogen oxide sensors, hydrocarbon sensors, carbon monoxide sensors, and hydrogen sensors.

The gas sensor comprises one or more electrochemical cells (i.e., an electrolyte disposed between two electrodes), with a heater in thermal communication with the electrochemical cell(s). In a single cell design, a porous protective layer is typically disposed adjacent to an outer electrode, with a reference gas chamber disposed in fluid communication with both a reference electrode and the atmosphere around the gas sensor, i.e., the air and, optionally the exhaust gas. In order to seal the reference gas chamber from exposure to the exhaust gas, it may optionally be hermetically sealed. Additionally, one or more gas diffusion limiters may be employed within the reference gas chamber as an alternative to or in conjunction with a hermetic seal..

Referring to Figure 1, the sensor element 10 is illustrated. The exhaust gas (or outer) electrode 20 and the reference gas (or inner) electrode 22 are disposed on opposite sides of, and adjacent to, a solid electrolyte layer 30 creating an electrochemical cell (20/30/22). On the side of the exhaust gas electrode 20 opposite solid electrolyte 30 is a protective insulating layer 40 having a dense section 44 and a porous section 42 that enables fluid communication between the exhaust gas electrode 20 and the exhaust gas. Meanwhile, disposed on the side of the reference electrode 22, opposite the solid electrolyte 30, is a reference gas channel 60 that is in fluid communication with the reference electrode 22 and optionally with the ambient atmosphere and/or the exhaust gas. Disposed on a side of the reference gas channel 60, opposite the reference electrode 22, is a heater 62 for maintaining sensor element 10 at the desired operating temperature. Typically disposed between the reference gas channel 60 and the heater 62, as well as on a side of the heater opposite the reference gas channel 60, are one or more insulating layers 50, 52.

Insulating layers 50, 52, and any support layers, are typically capable of: providing structural integrity (e.g., effectively protecting various portions of the gas sensor from abrasion, vibration, and the like, and providing physical strength to the sensor); and physically separating and electrically isolating various components. The insulating layer(s), which can be formed using ceramic tape casting methods or other methods such as plasma spray deposition techniques, screen printing, stenciling and others conventionally used in the art, can each be up to about 200 microns thick, with a thickness of about 50 microns to about 200 microns preferred. Typically these insulating layers comprise a dielectric material, such as alumina and the like. Since the materials employed in the manufacture of gas sensors preferably comprise substantially similar coefficients of thermal expansion, shrinkage characteristics, and chemical compatibility in order to minimize, if not eliminate, delamination and other processing problems, the particular material, alloy or mixture chosen for the insulating layer is dependent upon the specific electrolyte employed.

The electrolyte layer, which is preferably a solid electrolyte that can comprise the entire layer 30 or a portion thereof, can be any material that is

capable of permitting the electrochemical transfer of oxygen ions while inhibiting the physical passage of exhaust gases, has an ionic/total conductivity ratio of approximately unity, and is compatible with the environment in which the gas sensor will be utilized (e.g., up to about 1,000°C). Possible solid electrolyte materials can comprise any material conventionally employed as sensor electrolytes, including, but not limited to, zirconia which may optionally be stabilized with calcium, barium, yttrium, magnesium, aluminum, lanthanum, cesium, gadolinium, and the like, as well as combinations comprising at least one of the foregoing. For example, the electrolyte can be alumina and yttrium stabilized zirconia. Typically, the solid electrolyte, which can be formed via many conventional processes (e.g., die pressing, roll compaction, stenciling and screen printing, tape casting techniques, and the like), has a thickness of up to about 500 microns, with a thickness of approximately 25 microns to about 500 microns preferred, and a thickness of about 50 microns to about 200 microns especially preferred.

In some embodiments, a porous electrolyte may also be employed. The porous electrolyte should be capable of permitting the physical migration of exhaust gas and the electrochemical movement of oxygen ions, and should be compatible with the environment in which the gas sensor is utilized. Typically, a porous electrolyte has a porosity of up to about 20%, with a median pore size of up to about 0.5 microns, or, alternatively, comprises a solid electrolyte having one or more holes, slits, or apertures therein, so as to enable the physical passage of exhaust gases. Commonly assigned U.S. Patent No. 5,762,737 to Bloink et al., which is hereby incorporated in its entirety by reference, further describes porous electrolytes that may be useful in the instant application. Possible porous electrolytes include those listed above for the solid electrolyte.

It should be noted that the electrolyte 30, as well as the protective material 40, can comprise entire layer or any portion thereof; e.g. they can form the layer, be attached to the layer (protective material/electrolyte abutting a dielectric material), or disposed in an opening in the layer (protective material/electrolyte can be an insert in an opening in a dielectric material layer). The latter arrangement eliminates the use of excess electrolyte and protective material, and reduces the

size of gas sensor by eliminating layers. Any shape can be used for the electrolyte and protective material, with the size and geometry of the various inserts, and therefore the corresponding openings, is dependent upon the desired size and geometry of the adjacent electrodes. It is preferred that the openings, inserts, and electrodes have a substantially similar geometry.

Disposed on opposites sides of the electrolyte 30, and in ionic communication therewith, are electrodes 20, 22. These electrodes can comprise any catalyst capable of ionizing oxygen, including, but not limited to, metals such as platinum, palladium, osmium, rhodium, iridium, gold, and ruthenium; metal oxides such as zirconia, yttria, ceria, calcia, alumina and the like; other materials, such as silicon, and the like; and mixtures and alloys comprising at least one of the foregoing catalysts. As with the electrolyte, the electrodes 20, 22 can be formed using conventional techniques. Some possible techniques include sputtering, chemical vapor deposition, screen printing, and stenciling, among others. If a co-firing process is employed for the formation of the sensor, screen printing the electrodes onto appropriate tapes is preferred due to simplicity, economy, and compatibility with the co-fired process. For example, reference electrode 22 can be screen printed onto insulating layer 50 or over the solid electrolyte 30, while exhaust electrode 20 can be screen printed over solid electrolyte 30 or on protective layer 40. Electrode leads 15 and vias (not shown) in the insulating and/or electrolyte layers are typically formed simultaneously with electrodes.

In order to reduce offset voltage, i.e., reduce impedance, the size (e.g., diameter) of the reference electrode can be different, preferably larger, than the diameter of the exhaust gas electrode. Previously it was believed that the portion of the reference electrode which did not overlap the reference gas channel would be inactive. Consequently, the reference electrode, to minimize resistance, had a diameter substantially equivalent to the width of the reference gas channel. It has been discovered, however, that a reduction in impedance can be obtained by increasing the size of the reference electrode with the ultimate size merely bounded by the size of the layer upon which the electrode is disposed. For example, the reference electrode can have a diameter which is up to about 95% of the width ("w") of the insulating layer, with a width about 60% to about 85% of the width of

the support layer preferred, and a width of about 70% to about 80% of the width of the support layer especially preferred. Essentially, the reference electrode has a surface disposed on a side of the reference electrode opposite the electrolyte. At least a portion of the reference electrode surface is in physical contact with the reference gas channel. The portion of the surface in contact with the reference gas channel can be up to about 90% of the reference electrode surface area, with about 75% or less, about 50% or less, about 25% or less, and even 15% or less, of the reference electrode surface area acceptable.

In order to ensure sufficient diffusion of the reference gas through the reference electrode, the reference electrode preferably has a sufficient porosity such that the mass diffusion, i.e., the combined gas and solid transport, of the reference gas to the triple points is not reaction limiting. In other words, there is sufficient oxygen available at the triple points such that the sensor readings are not affected. As is known in the art, the reference electrode porosity can be controlled via a number of factors including the size of the particles employed to form the electrode, the use of fugitive materials, etc. Typically the electrodes comprise any catalyst capable of ionizing oxygen, including, but not limited to, precious metal catalysts such as platinum, palladium, gold, rhodium, and the like, other metals and metal oxides, and other conventional catalysts including mixtures and alloys comprising at least one of these materials. In order to ensure the desired porosity, the catalyst employed for the reference electrode preferably has an average particle size of about 10 microns (μ) or less.

Disposed in fluid communication with the reference electrode 22 is the reference gas channel 60. This channel can be contained within the sensor, can be in fluid communication with air or other reference gas external to the sensor with a hermetic seal to prevent poisoning by the exhaust gas, or can be in fluid communication with the exhaust gas. Production of the reference gas channel can be accomplished via mechanical cutting-in duck, screen-printing fugitive material (such as carbon which can be burned off at high temperature), porosity controlled coating layering, laser drilling holes, and the like. For example, the reference gas channel 60 can be formed by depositing a fugitive material (e.g., carbon base material such as carbon black), between reference electrode 22 and layer 50 such

that upon processing the carbon burns out, and leaves a void. Optionally, the reference gas channel 60 can have a controlled geometry to impart diffusion limitation therein (e.g., a small cross-sectional area which inhibits exhaust gas migration into the channel while allowing escape of excess oxygen), and/or can comprise an oxygen storage material to ensure sufficient oxygen supply to the reference electrode 22. Some examples of possible oxygen storage materials include precious metals, as well as alloys and mixtures comprising at least one precious metal.

On a side of the reference gas channel 60 opposite the reference electrode 22, typically disposed between two insulating layers, e.g., 50, 52, is a heater 62 that is employed to maintain the sensor element at the desired operating temperature. Heater 62 can be any conventional heater capable of maintaining the sensor end at a sufficient temperature to facilitate the various electrochemical reactions therein. The heater 62, which is typically platinum, alumina, palladium, and the like, as well as mixtures and alloys comprising at least one of the foregoing metals, or any other conventional heater, is generally screen printed onto a substrate to a thickness of about 5 microns to about 50 microns.

As with the heater 60, other conventional gas sensor components and/or materials can be employed, such as ground plane(s), lead gettering layer(s), additional support layer(s), additional electrochemical cell(s), vias, contact pads, protective coating(s), and the like. For example, protective coatings (e.g., spinel, alumina, magnesium aluminate, and the like, as well as combinations comprising at least one of the foregoing coatings), can be disposed over the sensor or merely over one or more of the outer layers (i.e., protective layer 40 and/or insulating layer 52).

Basically, formation of the gas sensor can be accomplished in any conventional fashion; e.g., forming the individual layers of the sensor, firing the layers, and stacking the layers to for the sensor, or forming the green layers, stacking the layers, and co-firing to produce the sensor. For example, a protective layer, three insulating layers, an electrolyte layer, and a porous layer are formed using a doctor blade tape forming method. The desired vias are formed in these layers accordingly. Holes are also formed in the protective layer and the

electrolyte layer using a punching technique. Inserts are formed from the electrolyte layer and the porous layer using a similar punching technique, wherein the inserts size and geometry is preferably substantially the same as the hole size and geometry. The porous insert is then disposed into the protective layer hole and the electrolyte insert is disposed in the insulating layer hole. An exhaust gas electrode is then screen printed over the electrolyte with a lead printed across the insulating layer. On another insulating layer a fugitive material is sputtered across the layer and then a reference electrode is screen printed at one end of the insulating layer in fluid communication with the fugitive material, and a lead is printed down the insulating layer. On the final insulating layer a heater with heater leads is printed. The layers are then stacked accordingly (e.g., see Figure 1), and contacts are formed on the outer surfaces of the sensor. The sensor can then optionally be dipped to apply a protective coating on the sensor. Finally, the green sensor is laminated at about 2,000 to about 4,000 pounds per square inch (psi) and at temperatures up to about 70°C or so, singulated, and co-fired at atmospheric pressure and temperatures up to about 1550°C or so.

Referring to Figure 2, insulating layer 50 with reference gas channel 60 and reference electrode 22 disposed thereon is illustrated. As is evident from the figure, the reference electrode 22 is substantially larger than the reference gas channel 60, with the channel 60 only overlapping less than about 20% of the reference electrode 22.

A cross-sectional view of a sensing element employing the reference electrode of Figure 2 is presented in Figure 3. Figure 3 illustrates that the reference electrode 22 does not have to be limited in size by the reference gas channel 60 and that the electrodes do not need to have the same diameter. Due to the chemistry of the reaction, it is not necessary to increase the size of the exhaust gas electrode 20 (actually, increasing the size merely increases cost with little to no benefit) while increasing the size of the reference electrode 22 substantially reduces the impedance of the sensor. Essentially, by increasing the size of the reference electrode, the impedance can be reduced by greater than 25% versus conventional sensors having reference electrodes having about 95% overlap with the air reference channel or greater. Consequently, the reference electrode 22 can

be a different size than the exhaust gas electrode 20, with a larger reference electrode preferred.

The following examples are merely intended to further illustrate the invention and not to limit the scope thereof.

EXAMPLE 1

Alumina and yttria-doped zirconia were mixed with binders, plasticizers, and solvents. They were roll-milled into a slurry. The slurry was casted into thick film tapes by doctor blade tape casting method. Platinum inks and carbon inks were screen printed onto the tapes in the structure as shown in Figure 1. Protective layer 40 was a composite layer of alumina and porous tape which contained various mixtures of carbon, zirconia, and alumina. Layers 50, 52 were alumina tapes for insulation and support. Layer 30 was the solid electrolyte layer (i.e., yttria-doped zirconia). Screen prints 20, 22 were the exhaust and reference electrodes, respectively. These prints are platinum with various additives (i.e., zirconia, carbon). Screen print 62 is the integrated resistive heater. It is a platinum print with alumina powder added. Screen print 60 is a carbon print which is fugitive material. Therefore, after sintering, this is an open chamber.

After each layer was processed, they were stacked properly, laminated, singulated, and fired at 1,500°C.

The impedance of the sample was measured by applying a voltage to the heater until a temperature of about 800°C to about 900°C was reached. A small, constant bias voltage was then applied to the electrochemical cell, and the resulting current was measured. Figure 5 is a graphical representation of the results (line 53), along with the theoretical calculations (line 55) for what the impedance should be at the corresponding temperatures. The equation for the DC impedance of an electrochemical cell is set forth in Equation (I) as follows:

$$R_{zirconia} = \rho * (L/A) \qquad (I)$$

where: ρ – resistivity of electrolyte
L – thickness of electrolyte
A – area of electrode

The resistivity factor (ρ) is described by the following Equation (II):

$$\rho = 10^{-5}\left(e^{\frac{Lev}{kT}}\right)T \qquad \text{(II)}$$

where: T – temperature (Kelvin)
K – $8.63*10^{-5}$ (Boltzmann's constant)
Lev – activation energy of zirconia (fundamental property of material)
10^5 – ionic mobility

The above Equations I and II assume that the entire reference electrode will be active. Yet, only a small amount of the reference electrode must be exposed to the reference gas channel, and the reference electrode will not diffusion-limit the flow of oxygen. Therefore, essentially all of the reference electrode area is active, and the above equations apply. The reference gas channel can be created as small as possible while the reference electrode can be increased, thus lowering the electrolyte resistance and the reference electrode polarization.

EXAMPLE 2

Two sensors were formed using conventional techniques: a wide reference electrode sensor having a 3 mm diameter disk (area of about 7 mm^2) (Sample A); and a conventional sensor having a "thin" reference electrode (0.5 millimeters (mm) wide and 5 mm long rectangle (area of about 2.5 mm^2) (Sample B); both sensors had a reference gas channel which was about 0.6 mm wide and about 5.5 mm long. The remainder of the sensor components, protective layer, insulating layers, exhaust gas electrode, heater, electrolyte, etc., which were conventional, were the same for both sensors.

Resistance of these sensors was then determined. First, the sensors were maintained in a fuel rich environment (e.g., an air to fuel (A/F) ratio of about 13.3) to generate an electromotive force (emf). Next, a small load resistor (about 50 kiloohms (kΩ)) was attached to the sensor, demanding a current of:

$$I = \frac{V_s}{R_s + R_l}$$

where: V_s = emf
R_s = internal sensor resistance
R_l = input impedance of ECM

R_s can be calculated from the voltage divides between the resistor and the internal resistance (impedance) of the sensor, the open circuit voltage, the loaded voltage, and the know input impedance of engine control module (ECM). The voltage divider Equation (III) is:

$$V_l = V_s\left(\frac{R_l}{R_l + R_s}\right) \qquad \text{(III)}$$

where: V_l = loaded voltage

With testing performed under the same conditions, (e.g., temperature and engine conditions), Sample A had a mean resistance of 3,400 ohms, while Sample B had a mean resistance of 4,800 ohms. Basically a sensor was produced having a reduced mean resistance, e.g., below about 4,000 Ω, with below about 3,500 Ω preferred, and about 3,400 Ω or less especially preferred.

Artisans believed that in order for the reference electrode to be effective, it could not be larger than the air reference gas channel in the area of that electrode. Basically, the reference electrode and reference gas channel needed to substantially overlap (e.g., greater than about 95%). It was believed that the portion of the reference electrode, which did not overlap the reference gas channel, would be inactive. This belief posed particular problems for co-fired sensors since the size of the reference gas channel was limited. Essentially, due to the subsequent processing to volatilize the fugitive material (laminating, sintering, and the associated temperatures and pressures), if the channel was too large it would deform (e.g., collapse, pinch off, or the like). Consequently, the size of the reference gas channel was limited due to processing limitations, and hence it was

believed that the size of the reference electrode was limited by the size of the channel. Contrary to that belief, however, it has been discovered that, since only a small amount of the reference electrode needs to be exposed to the reference gas channel in order to attain the desired reference gas supply to the reference electrode, the size of the reference electrode is not dependent upon the size of the reference gas channel. Consequently, the reference electrode size can be optimized based upon the overall sensor size (e.g., width of the layer upon which the electrode is disposed). The resulting sensor possesses a reduced electrochemical cell impedance, and performance parameters including rich exhaust voltage, light-off time, and loading down the sensor with the input impedance are improved. While preferred embodiments have been shown and described, various modifications and substitutions may be made thereto without departing from the spirit and scope of the invention, including the use of the geometries taught herein in other conventional sensors. Accordingly, it is to be understood that the apparatus and method have been described by way of illustration only, and such illustrations and embodiments as have been disclosed herein are not to be construed as limiting to the claims.

We claim:

CLAIMS

1. A gas sensor, comprising:

a first electrode and a reference electrode with an electrolyte disposed therebetween, wherein the first electrode and the reference electrode are in ionic communication, wherein the reference electrode has a surface on a side of the reference electrode opposite the electrolyte and the surface has a surface area; and

a reference gas channel in fluid communication with the reference electrode, wherein at least a portion of the surface of the reference electrode physically contacts at least a portion of the reference gas channel, and wherein the portion of the reference electrode in physical contact with the reference gas channel is less than about 90% of the surface area.

2. A gas sensor as in Claim 1, wherein the portion of the reference electrode in physical contact with the reference gas channel is less than about 75% of the surface area.

3. A gas sensor as in Claim 2, wherein the portion of the reference electrode in physical contact with the reference gas channel is less than about 50% of the surface area.

4. A gas sensor as in Claim 3, wherein the portion of the reference electrode in physical contact with the reference gas channel is less than about 25% of the surface area.

5. A gas sensor as in Claim 4, wherein the portion of the reference electrode in physical contact with the reference gas channel is less than about 15% of the surface area.

6. A gas sensor as in Claim 1, further comprising a heater disposed in thermal communication with the reference electrode.

7. A gas sensor as in Claim 1, wherein the gas sensor has an impedance below about 4,000 Ω.

8. A gas sensor as in Claim 7, wherein the gas sensor has an impedance below about 3,500 Ω.

9. A gas sensor as in Claim 8, wherein the gas sensor has an impedance below about 3,400 Ω or less.

10. A gas sensor as in Claim 1, wherein a first electrode size is different than a reference electrode size.

11. A gas sensor as in Claim 10, wherein the first electrode size is smaller than the reference electrode size.

12. A method for forming a gas sensor, comprising:

disposing an outer electrode and a reference electrode on opposite sides of an electrolyte such that the outer electrode and the reference electrode are in ionic communication, wherein the reference electrode has a surface on a side of the reference electrode opposite the electrolyte;

disposing at least a portion of a fugitive material in physical contact with a portion of the reference electrode surface, wherein the reference electrode has a surface area and the portion of the reference electrode surface in physical contact with the fugitive material is less than about 90% of the surface area;

disposing a heater on a side of the fugitive material opposite the reference electrode to form a green sensor; and

co-firing the green sensor.

13. A method for forming a gas sensor as in Claim 12, wherein the portion of the reference electrode surface in physical contact with the fugitive material is less than about 75% of the surface area.

14. A method for forming a gas sensor as in Claim 13, wherein the portion of the reference electrode surface in physical contact with the fugitive material is less than about 50% of the surface area.

15. A method for forming a gas sensor as in Claim 14, wherein the portion of the reference electrode surface in physical contact with the fugitive material is less than about 25% of the surface area.

16. A method for forming a gas sensor as in Claim 15, wherein the portion of the reference electrode surface in physical contact with the fugitive material is less than about 15% of the surface area.

17. A method for forming a gas sensor as in Claim 12, wherein the gas sensor has an impedance below about 4,000 Ω.

18. A method for forming a gas sensor as in Claim 17, wherein the gas sensor has an impedance below about 3,500 Ω.

19. A method for forming a gas sensor as in Claim 18, wherein the gas sensor has an impedance below about 3,400 Ω or less.

20. A method for forming a gas sensor as in Claim 12, wherein the first electrode and the reference electrode are of different sizes.

FIG. 1

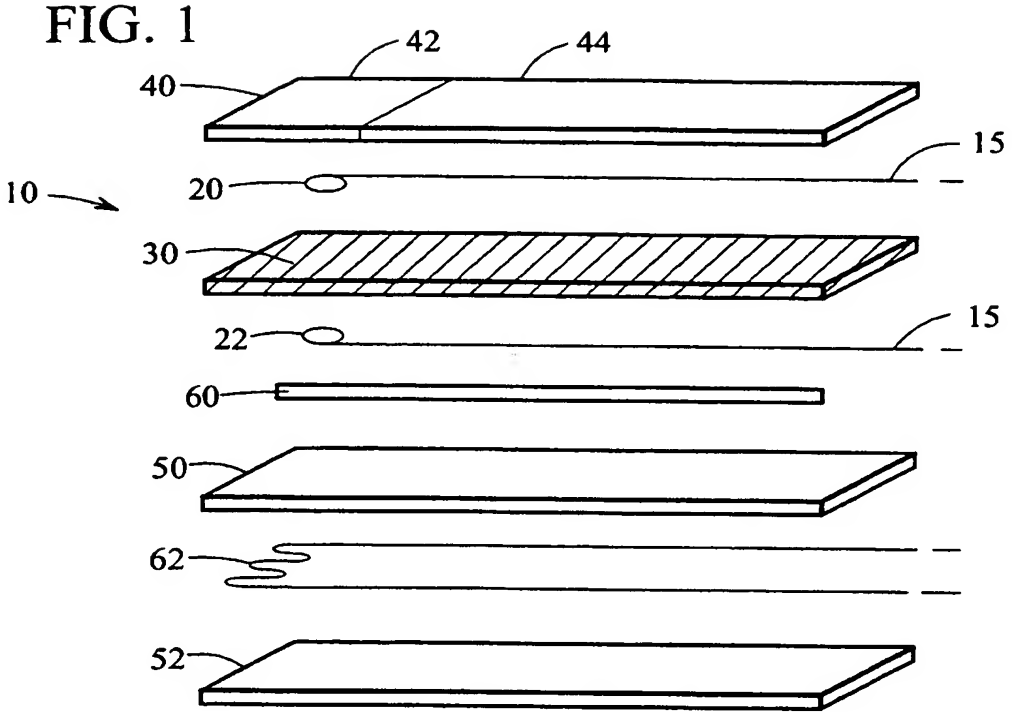


FIG. 2

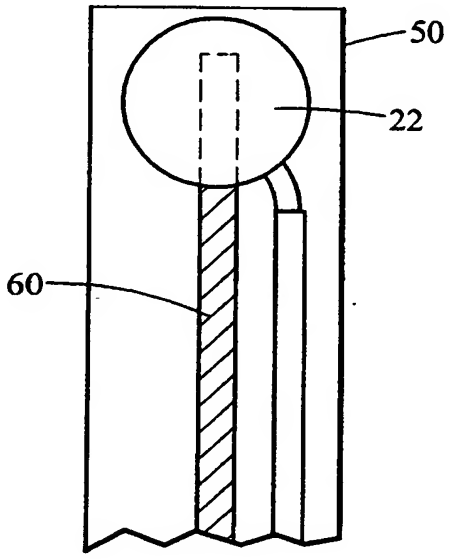
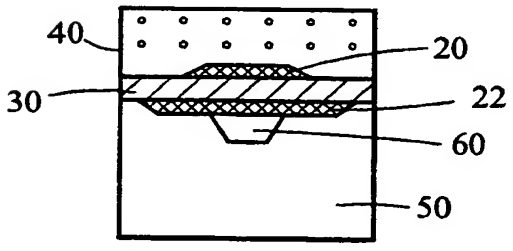
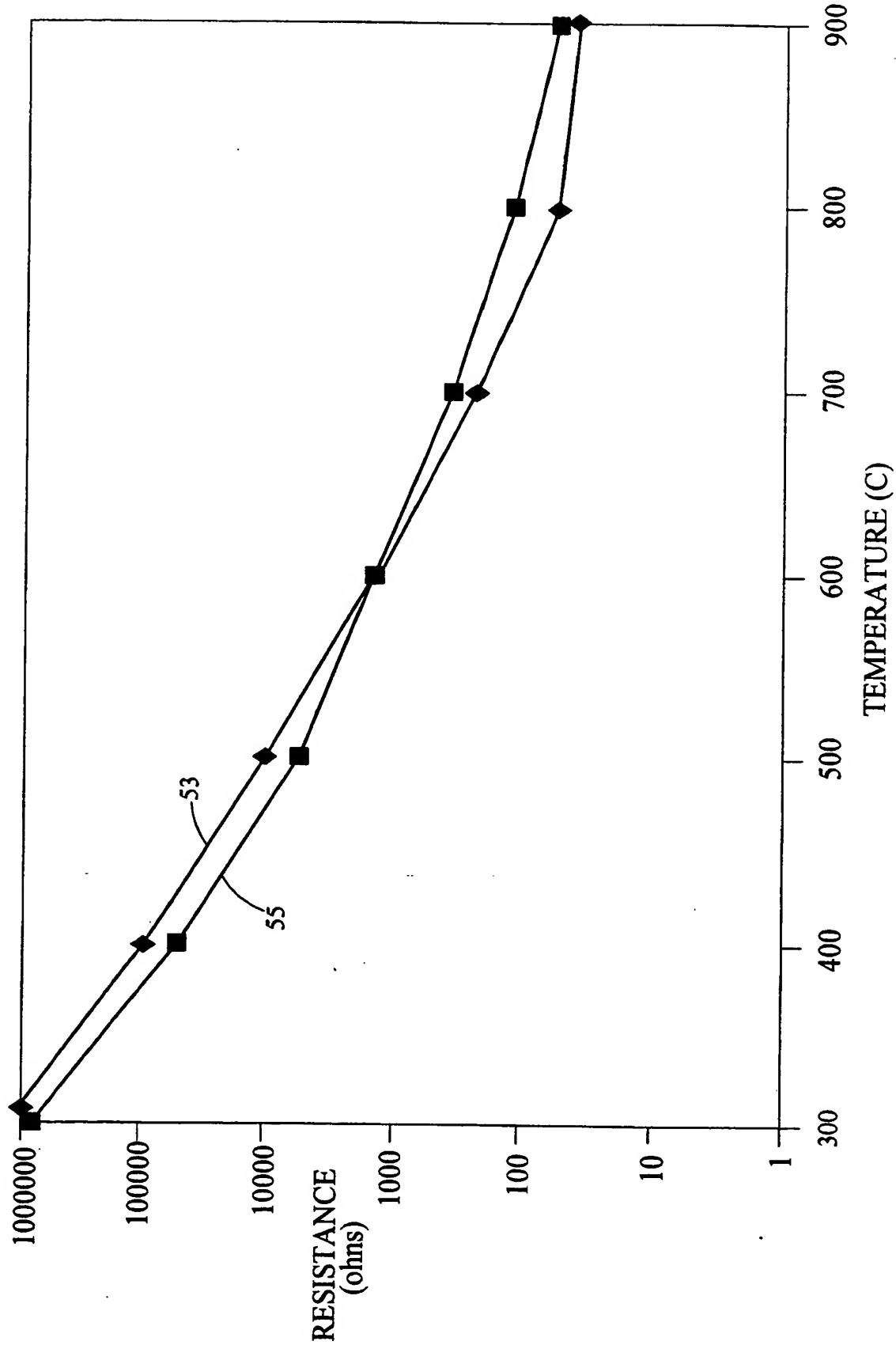


FIG. 3

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10000
1000
100
10
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RESISTANCE (ohms)
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400
500
600
700
800
900
TEMPERATURE (C)
53
55

FIG. 4

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 00/29147

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 G01N27/407

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 G01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	DE 198 35 766 A (BOSCH GMBH ROBERT) 17 February 2000 (2000-02-17) column 2, line 29 - line 38; figure 3 abstract	1,12
A	US 5 304 294 A (WANG DA Y ET AL) 19 April 1994 (1994-04-19) abstract column 2, line 18 - line 53; figure 1	1-20
A	US 4 657 659 A (MASE SYUNZO ET AL) 14 April 1987 (1987-04-14) abstract column 4, line 9 - line 43; figure 1	1-20

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
29 January 2001	06/02/2001

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Kempf, G

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INTERNATIONAL SEARCH REPORT

information on patent family members

Inter[illegible]nal Application No
PCT/US 00/29147

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